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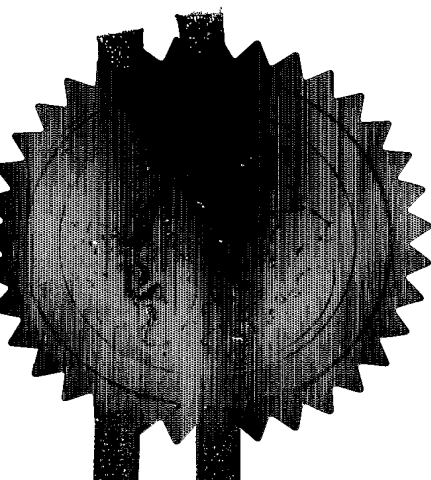
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02 MAR 2004



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1. Your reference 11390P6 GB/AB

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0404658.7

3. Full name, address and postcode of the or of each applicant (underline all surnames)

07921075005

Patents ADP number (if you know it)

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If the applicant is a corporate body, give the country/state of its incorporation

Netherlands

4. Title of the invention

Enzymes as Corrosion Inhibitors by Removal of Oxygen Dissolved in Water

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Andrew Stephen BROWN
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Dansom Lane
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HU8 7DS
United Kingdom

077999521001

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Country

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Date of filing
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:


Yes


- a) any applicant named in part 3 is not an inventor, or
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- See note (d))

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Description 12 

Claim(s) 1 

Abstract --

Drawing(s) --


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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

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Request for substantive examination (*Patents Form 10/77*)

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Any other documents (*please specify*)

FS1

11.

I/We request the grant of a patent on the basis of this application.

Signature 

Date

Andrew S BROWN

27 February 2004

12. Name and daytime telephone number of person to contact in the United Kingdom

Andrew S BROWN (01482) 582411

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DUPLICATE

5 ENZYMES AS CORROSION INHIBITORS BY REMOVAL OF OXYGEN
 DISSOLVED IN WATER

 The invention relates to a new process for water de-
oxygenation, for application in aerosol products. The
10 process involves the use of an enzymatic system based on
an oxidase enzyme a substrate for the oxidase enzyme and
catalase. These two enzymes consume oxygen by a two step
reaction with the substrate and hydrogen peroxide, which
is formed in the first reaction.

15 Corrosion reactions take place in the presence of
oxygen, oxygen dissolved in water is responsible for can
corrosion in aqueous based formulations within aerosol
containers. Currently a number of techniques are used to
20 minimise corrosion in aerosol cans, for example, by the
use of corrosion inhibitors or by an oxygen displacement
process using nitrogen gas. We have found that corrosion
is severely retarded if oxygen is substantially removed
from the water present in the aerosol can.

25 Examples of products found in aerosol cans are air
care products, household products, fabric care, waxes,
polishes, insecticides, ironing aids, fabric refreshers
and carpet cleaners.

30 The aerosol canister is metal, preferably steel or
tin coated steel.

 The world market trend is to move towards aerosol
35 formulations containing more water. This is due mainly to
regulatory issues: the reduction of the volatile organic

5 content (VOC) level in aerosol products has involved a reduction in the amount of solvent of many products and an increase in the water content.

10 When aerosol compositions contain less than 50 ppm of water, corrosion of the aerosol can is not generally a serious problem. However, if the water content is more than 50 ppm in the aerosol composition then corrosion is more likely to occur.

15 Many corrosion inhibitor systems have been developed for facing these new regulatory requirements. Examples of these products are borates, benzoates, molybdate, special surfactants (such as sodium lauroyl sarcosinate), sodium nitrite and morpholine and silicates. Usually an
20 acceptable control of the corrosion during the product life of the aerosol canister (around 2 years) is built in to the composition. The above corrosion inhibitors tend to interact with the aerosol canister's surface providing protection against corrosion.

25 There also can be negative effects of corrosive detinning on the performance of the product. The yellow tin corrosion complex may remain especially when sprayed onto white surface. White fabrics or carpets can remain
30 coloured by the liquids of aged aerosol products. Other considerations relate to certain stains like coffee, tea and wine that contain cationic metals. These metals can form brown coloured complexes with tin hydroxyl, causing an evident negative effect of the cleaning formulation
35 onto overall cleaning performance.

5 Therefore, there is a need to identify better ways
to prevent corrosion in aerosol canisters.

Corrosion is an electrochemical process. All
corrosion reactions are started by the presence of water
10 and oxygen. Oxygen is a direct participant in the
corrosion reaction, acting as a cathode-accepting
electron.

Dissolved oxygen present in water based formulations
15 within aerosols is one of the most important factors
influencing the rate of corrosion for all metals.

Many corrosion inhibitors have been identified in
the prior art, but none really halt dissolution of the
20 tin layer in tin-plated aerosol cans over the two years
standard can life, they merely slow it down. Even resin
lacquered tin-plated cans generally need an effective
corrosion inhibitor system.

25 T.Godfrey, J.Reichelt: Industrial Enzymology, Nature
Press 1983 - Chapter 4.2: G.Richter - Glucose Oxidase, US
5,980,956, EP 0818960 & EP 0835299 describe the use in
the food industry and especially in canned soft drinks
industry of an enzymatic system based on glucose oxidase
30 and catalase as an antioxidant primarily to prevent
changes in colour and flavour of foods products both
during processing and in storage.

US 4,414,334 describes the use of alcohol oxidase
35 and catalase to remove oxygen dissolved in aqueous

5 liquids and discloses the use of such systems in
foodstuffs and water distribution systems.

10 Currently a vacuum process is used to remove oxygen
during aerosol product manufacture, which does reduce the
oxygen content in the aerosol can. The reduction is
anyway just in the aerosol can head space and has little
effect on the deoxygenation of the liquid phase. For
liquid phase deoxygenation currently used is a nitrogen
stripping process that is quite expensive. The process of
15 the present invention can reduce the oxygen content in
the aerosol can during manufacturing and even further,
during product storage.

20 We have found that the use of an oxidase enzyme and
a substrate for the oxidase enzyme combined with catalase
effectively reduces the rate of corrosion in aerosol cans
by reducing almost to zero the concentration of oxygen
dissolved in the water.

25 The process of the invention is particularly
effective at neutral and acidic pH. The deoxygenating
process requires a longer time at alkaline pH: this is
not necessarily a problem since the enzymatic system will
continue to work over time if placed in the aerosol
30 product.

Other advantages of enzymes are that they are very
effective even at low concentration, starting from 0.01
ppm of enzyme and 50 ppm of substrate. The enzymes are
35 also compatible with aerosol formulations and have a low
impact on the overall formulation cost.

5 We present as a feature of the invention an aerosol product comprising a sealed metal canister containing an aerosol composition comprising an oxidase enzyme, a substrate for the enzyme and catalase.

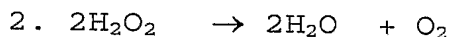
10 Suitable oxidase enzymes are those classified under enzyme classification E.C.1.1.3 (Acting on the CH-OH group of donors with oxygen as acceptor) and include one or more of the following. Not all enzymes produce hydrogen peroxide as a product of the reaction. Therefore
15 in a preferred feature of the invention when such enzymes are used the presence of catalase is not required, for example nucleoside oxidase.

20 Preferred enzymes are selected from one or more of the following; Malate oxidase, Glucose oxidase, Hexose oxidase, Cholesterol oxidase, Aryl-alcohol oxidase, L-gulonolactone oxidase, Galactose oxidase, Pyranose oxidase, L-sorbose oxidase, Pyridoxine 4-oxidase, Alcohol
25 oxidase, Catechol oxidase, (S)-2-hydroxy-acid oxidase, Ecdysone oxidase, Choline oxidase, Secondary-alcohol oxidase, 4-hydroxymandelate oxidase, Long-chain-alcohol oxidase, Glycerol-3-phosphate oxidase, Xanthine oxidase, Thiamine oxidase, L-galactonolactone oxidase, Cellobiose
30 oxidase, Hydroxyphytanate oxidase, Nucleoside oxidase, N-acylhexosamine oxidase, Polyvinyl-alcohol oxidase, Methanol oxidase, D-arabinono-1,4-lactone oxidase, Vanillyl-alcohol oxidase, Nucleoside oxidase, D-mannitol oxidase and Xylitol oxidase.

(

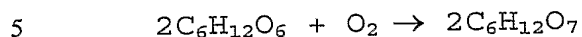
20

The reaction is:



35

Total reaction:



By forcing the equilibrium of the reaction by an excess of substrate to the oxidase enzyme, it is possible to end up with a final oxygen content close to zero.

10

Therefore, the concentration of substrate needed in order to increase the velocity of the first reaction is ideally greater than the K_m of the enzyme selected (K_m is the Michael's constant and is the affinity of the enzyme for the substrate, i.e. the concentration at which 50% of the enzyme binding sites are occupied). Typical K_m 's are 10^{-1} M to 10^{-6} M.

20 An important feature of the invention is a substrate for the oxidase enzyme used, this may already be present in the composition to be packaged in the aerosol canister or it might. A preferred substrate is D-glucose.

25 The performance of the new corrosion inhibitor system has been evaluated first by measuring the dissolved oxygen reduction (Oxy-meter) in a typical conditions and then by a quick method for the evaluation of corrosion, the jar method, using as fill formulation using tap water treated or not with the enzymatic system on a standard epoxy coated piece of aerosol can.

30

OXY-METER EVALUATION

A 5L glass beaker is used in this test.
35 4L of tap water are added into the beaker and warmed to 40°C.

5 pH of the solution is measured and adjusted to desired value. Dissolved oxygen (DO mg/L) pH and Temperature (°C) are measured through an Oxy-Meter YSI 556 MPS.

10 The time zero DO value is collected, D-Glucose is added to the solution and immediately after the enzymatic system is dosed.

The reaction is then followed constantly reading the DO value until it reaches a plateau value.

15

The system is open, so no control to oxygen intake from the air is considered.

JAR METHOD:

20

50 ml glass jars with screw plugs are used in this test.

25 A round piece of a can is cut and applied on the internal surface of the jar screw plug. A cross is cut by a blade on the can piece in order to simulate possible defects on the can walls.

A poly tetra fluoroethylene gasket is also applied on the plug in order to guarantee a good sealing system. The jar
30 is filled with the testing formula and it is stored in the inverted position to obtain the contact between the liquid formula and the tin plated can piece applied on the plug.

35 The storage is carried out at different temperature (20°C, 40°C and 50°C) for several days up to 1 month. The

- 5 storage situation is monitored after 1 day, 1 week, 2 weeks, 1 months and compared to reference can pieces and liquids. The can piece appearance is recorded. A recording data table with the corresponding corrosion rating is reported below:

10

Corrosion Rating JM	Can piece appearance
0	No difference from reference
1	Low darkening along the cut lines
2	Darkening along the cut lines
3	Strong darkening on all the can piece area
4	Darkening on all the can piece area
5	Evident darkening on all the can piece area
6	Rust

EXAMPLES:

- 15 The liquid phases are typically prepared by mixing D-Glucose anhydrous to warm 40°C tap water, adjusting the pH to the desired value and then adding the enzymatic system to start the de-oxygenation reaction.

5

Table 1						
Components	Ref 1	Ref 2	Ref 4	Ref 5	Ref 6	Ref 7
	ppm	ppm	ppm	ppm	ppm	ppm
D-Glucose	60 (0.006%)	250 (0.025%)	500 (0.05%)	1000 (0.05%)	1000 (0.1%)	500 (0.05%)
OxyGo 1500	0.0125	0.05	0.1	0.2	0.2	0.1
Tap Water	to 100	to 100	to 100	to 100	to 100	to 100
PH	7	7.8	7.1	7.1	9.1	4.9

Table 2	
Component	Description of component
D-Glucose	D(+)-Glucose anhydrous >99.5% from Fluka
OxyGo 1500	Glucose Oxidase Enzyme with Catalase side activity from Genencor
NaOH	Sodium Hydroxide, 10% solution
H2SO4	Sulphuric Acid, 9% solution

EXAMPLE RESULTS:

- 10 The enzymatic corrosion inhibitor system has been tested for all formulations previously described in terms of the Oxy-meter evaluation and for formulation Ref.4, Ref.5, Ref. 6 and Ref.7 in terms of the Jar method. Evaluation of possible residue of H2O2 due to slow action of
- 15 catalase has also been done for formulation Ref.4, Ref.5, Ref.6 and Ref.7.

Results:

5

Product	DO (mg/L) at 40°C (Oxy-meter evaluation)			
	Time 0	30'	60'	90'
Ref 1	4.40	4.03	3.79	3.69
Ref 2	4.24	4.12	3.42	3.18
Ref 4	4.31	2.06	1.40	1.10
Ref 5	4.51	1.05	0.84	0.60
Ref 6	4.50	2.76	2.01	1.49
Ref 7	3.80	1.55	1.48	1.25

Product	Corrosion rating (Jar method)							
	1 day		1 week		2 weeks		1 month	
20°C	uncut	cut	uncut	cut	uncut	cut	uncut	cut
Ref 4	0	0	0	0	0	0	0	1
Ref 5	0	0	0	0	0	0	0	1
Ref 6	0	0	0	0	0	1	0	1
Ref 7	0	0	0	0	/	/	/	/
Tap Water	0	6	0	6	0	6	1	6

40°C	1 day		1 week		2 weeks		1 month	
	uncut	cut	uncut	cut	uncut	cut	uncut	cut
Ref 4	0	0	0	0	0	1	0	1
Ref 5	0	0	0	0	0	1	0	1
Ref 6	0	0	0	0	0	1	0	1
Ref 7	0	0	0	0	/	/	/	/
Tap Water	0	6	0	6	0	6	2	6

50°C	1 day		1 week		2 weeks		1 month	
	uncut	Cut	uncut	cut	uncut	cut	uncut	cut

Ref 4	0	0	0	0	0	0	0	1
Ref 5	0	0	0	0	0	1	0	2
Ref 6	0	0	0	0	0	2	0	2
Ref 7	0	0	0	0	/	/	/	/
Tap Water	0	6	0	6	0	6	2	6

5

Product	H2O2 % formation			
	10'	30'	60'	90'
Ref 4	0.01	0.00	0.00	0.00
Ref 5	0.00	0.00	0.00	0.00
Ref 6	0.03	0.00	0.00	0.00
Ref 7	0.01	0.00	0.00	0.00

10 The above results show that the two enzymatic reactions take place at the same time, so the H_2O_2 formed in the first step is immediately consumed in the second one. No issues coming from the formation of H_2O_2 is then foreseen.

15

5 CLAIMS

1. An aerosol product comprising a sealed metal canister containing an aerosol composition comprising an oxidase enzyme, a substrate for the enzyme and catalase.
10
2. An aerosol product as claimed in claim 1 wherein the aerosol composition comprises >50 ppm of water.
- 15 3. An aerosol product as claimed in either claim 1 or 2 wherein the oxidase enzyme is glucose oxidase and the substrate is D-glucose.
4. A method of deoxygenating an aerosol product comprising adding to an aerosol composition an oxidase enzyme, a substrate for the oxidase enzyme and catalase, filling an aerosol canister with the aerosol composition and propellant, and sealing the aerosol canister.
20
- 25 5. Use of an oxidase enzyme, a substrate for the oxidase enzyme and catalase as a corrosion inhibiting system for aerosol products.

